

# Statistical Thermodynamics in Chemistry and Biology

## 17. Physical kinetics: diffusion, permeation and flow

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March 7, 2016

# Forces drive molecules to flow

## This chapter:

- ▶ Many systems are **out of equilibrium** and are governed by **transport equations**.
- ▶ Molecules **diffuse**, transporting matter and heat.
- ▶ What are the **rates** at which molecules flow from one place to another?
- ▶ What forces drive them?
- ▶ See Appendix G for repetition of mathematics related to this chapter.

## Definition of flux

- The flux  $J$  is defined as the amount of material passing through a unit area per unit time,

$$J = \frac{cV}{A\Delta t} = \frac{cA\Delta x}{A\Delta t} = \frac{c\Delta x}{\Delta t} = cv$$

where  $c$  is the concentration and  $v$  is the velocity.

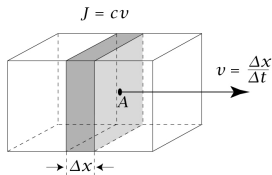
- Fluxes may arise from applied forces, here we assume a linear relation between the force,  $f$  and the velocity,  $v$ ,

$$f = \xi v$$

where  $\xi$  is the **friction coefficient**. This leads to

$$J = cv = \frac{cf}{\xi} = Lf$$

where  $L$  is a general proportionality constant.



## Fick's law

- ▶ At equilibrium for a single-phase system: the concentration is the same everywhere.
- ▶ Systems with concentration **gradients** are not in equilibrium.
- ▶ A fundamental empirical law, **Fick's law**, relates the flux to the concentration gradient,

$$J = -D \frac{dc}{dx} ; \quad \vec{J} = -D \vec{\nabla} c$$

or in general a force to the flow of particles.

- ▶ The proportionality constant,  $D$ , is termed the **diffusion coefficient**.
- ▶ Similarly, **Ohm's law** relates forces to electrical current, and **Fourier's law** relates forces to flow of heat,

$$J_q = -\kappa \frac{dT}{dx}$$

where  $\kappa$  is the **thermal conductivity**.

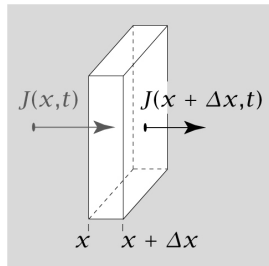
## Fick's second law

- ▶ The flux into a volume element does not need to be the same as out of the volume element since particles may be depleted or accumulated in the volume element.
- ▶ The increase of the amount of particles can be written as the difference between the number of particles entering and leaving the volume element,

$$A\Delta t (J(x, t) - J(x + \Delta x, t))$$

or as the change in number of particles with time at the center of the volume element,

$$A\Delta x \left( c\left(x + \frac{\Delta x}{2}, t + \Delta t\right) - c\left(x + \frac{\Delta x}{2}, t\right) \right)$$



# Fick's second law

## Part 2

- ▶ Taking the limits  $\Delta x \rightarrow dx$  and  $\Delta t \rightarrow dt$  gives,

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$

which is a fundamental equation, useful to remember.

- ▶ Substituting into *Fick's law*,

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) = D \frac{\partial^2 c}{\partial x^2}$$

which is called **Fick's second law** or the **diffusion equation**.

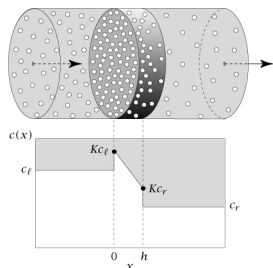
- ▶ In three dimensions,

$$\frac{\partial c}{\partial t} = -\vec{\nabla} \cdot \vec{J} = D \nabla^2 c$$

## Example 17.2: Diffusion through a membrane

- ▶ Many applications: cell membranes, polymer membranes in industry, etc., etc.
- ▶ The concentration to the left,  $c_l$ , is higher than to the right,  $c_r$ .
- ▶  $c_l$  and  $c_r$  are kept constant by addition and removal, respectively, of the species.
- ▶ Note the effect of the partition coefficient,  $K$ , in the graph.
- ▶ There is a driving force from left to right.
- ▶ Assume **steady-state**,

$$\frac{\partial c}{\partial t} = 0$$



## Example 17.2: Diffusion through a membrane

### Part 2

- ▶ Fick's second law becomes

$$\frac{\partial^2 c}{\partial x^2} = 0$$

- ▶ Integration gives

$$c(x) = A_1 x + A_2$$

where  $A_1$  and  $A_2$  are constants of integration.

- ▶ The **partition coefficient,  $K$** , gives us two concentrations in the membrane,

$$c(0) = Kc_l ; \quad c(h) = Kc_r$$

- ▶ For the concentration profile, we get

$$c(x) = \frac{K(c_r - c_l)}{h} x + Kc_l$$



## Example 17.2: Diffusion through a membrane

### Part 3

- ▶ The flux,  $J$ , becomes

$$J = -D \frac{\partial c}{\partial x} = \frac{KD}{h} (c_l - c_r) = \frac{KD}{h} \Delta c$$

- ▶ The **permeability**,  $P$ , of a membrane is defined as

$$P = \frac{KD}{h} = \frac{J}{\Delta c}$$

and the **resistance** as  $1/P$ .

# Diffusion of particles toward a sphere

- ▶ Example: micelle or a protein
- ▶ Assume **steady-state**.
- ▶ Spherical polar coordinates with no angular dependence (see Appendix G),

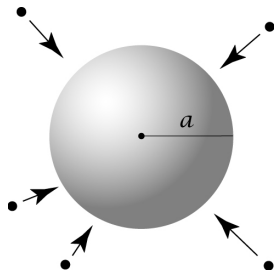
$$\nabla^2 c = \frac{1}{r} \frac{d^2 (rc)}{dr^2} = 0$$

- ▶ Integration gives,

$$c(r) = A_1 + \frac{A_2}{r}$$

- ▶ Two boundary conditions:  $A_1 = c_\infty$ , and the *absorbing boundary condition*,  $c(a) = 0$ ,

$$c(r) = c_\infty \left(1 - \frac{a}{r}\right)$$



# Diffusion of particles toward a sphere

## Part 2

- ▶ The flux,  $J$ , becomes

$$J(r) = -D \frac{dc}{dr} = \frac{-Dc_{\infty}a}{r^2}$$

- ▶ The **current**,  $I(a)$ , is the number of collisions per second at  $r = a$  (i.e flux times area),

$$I(a) = J(a)4\pi a^2 = -4\pi Dc_{\infty}a$$

# The Smoluchowski equation

- ▶ Sometimes particle flow is driven by both a concentration gradient and an applied force.
- ▶ The fluxes are **additive**,

$$J = -D \frac{\partial c}{\partial x} + \frac{cf}{\xi}$$

where  $\xi$  is a friction coefficient.

- ▶ Again combining with (see how we obtained Fick's second law),

$$\frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x}$$

gives the **Smoluchowski equation**,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \frac{f}{\xi} \frac{\partial c}{\partial x}$$

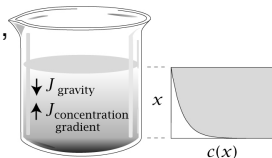
# The Einstein-Smoluchowski equation

- Start with the flux from the Smoluchowski eq.,

$$J = -D \frac{dc}{dx} + \frac{cf}{\xi}$$

and assume equilibrium,  $J = 0$ , (e.g. as in the figure),

$$D \frac{dc}{dx} = \frac{cf}{\xi} \Rightarrow D \frac{dc}{c} = \frac{f dx}{\xi}$$



- Assume a reversible work,  $w = - \int f dx$ ,

$$D \ln \frac{c(x)}{c(0)} = - \frac{w(x)}{\xi} \Rightarrow \frac{c(x)}{c(0)} = e^{-\frac{w(x)}{\xi D}}$$

- An equilibrium system must also follow a Boltzmann distribution, which gives the Einstein-Smoluchowski equation

$$\frac{c(x)}{c(0)} = e^{-\frac{w(x)}{k_B T}} \Rightarrow D = \frac{k_B T}{\xi}$$

## Ex. 17.7. Diffusion coupled to a chemical reaction

- Assuming a chemical reaction (empirical relation),

$$\frac{dc}{dt} = -k_{rx} c$$

which works as a *sink* (in contrast to a *source*).

- Fick's second law becomes,

$$\frac{dc}{dt} = D \left( \frac{\partial^2 c}{\partial x^2} \right) - k_{rx} c = 0$$

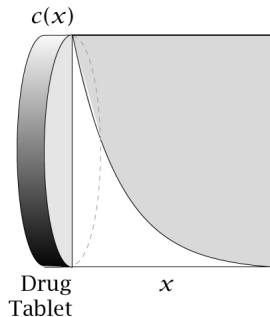
where we have assumed steady state,

$$\frac{dc}{dt} = 0.$$

- The general solution,

$$c(x) = A_1 e^{-ax} + A_2 e^{ax}$$

where  $a = \sqrt{\frac{k_{rx}}{D}}$



## Diffusion coupled to a chemical reaction, part 2

- ▶ Boundary condition:  $c_{\infty} = 0$  (everything has disappeared in the reaction) gives  $A_2 = 0$ ,

$$c(x) = c(0)e^{-x\sqrt{\frac{k_{rx}}{D}}}$$

- ▶ The flux at the surface,  $J(0)$ , may be calculated as,

$$J(x) = -D\frac{dc}{dx} = c(0)D\sqrt{\frac{k_{rx}}{D}}e^{-x\sqrt{\frac{k_{rx}}{D}}}$$

and

$$J(0) = c(0)\sqrt{Dk_{rx}}$$

- ▶ Using the example of a drug tablet, the drug is released faster if  $D$  or  $k_{rx}$  are high.

# Onsager reciprocal relations

- ▶ If two "gradients" are applied to a system, e.g. a temperature gradient drives a heat flow and a voltage difference generates an electrical current, these processes are **not independent**. In general,

$$J_1 = L_{11}f_1 + L_{12}f_2 ; \quad J_2 = L_{21}f_1 + L_{22}f_2$$

- ▶ The coupling elements,  $L_{12}$  and  $L_{21}$ , tell us that e.g. a voltage difference also generates a heat flow.
- ▶ Onsager showed that  $L_{12} = L_{21}$ , and are called **Onsager reciprocal relations**.
- ▶ The coupling elements,  $L_{ij}$ , are probably small (negligible) in many cases, but when they are substantial they may lead to novel phenomena and functional materials.
- ▶ Many potential applications, e.g. thermoelectricity



# Summary

- ▶ Introduction to nonequilibrium statistical thermodynamics.
- ▶ Primarily discussed diffusion (Fick's laws), but many other transport processes exist.
- ▶ Extended to coupled processes through Onsager reciprocal relations.
- ▶ For the future: *TKJ4200 Irreversible thermodynamics* (Prof. Signe Kjelstrup)

## Exam June 2012 - Exercise 2

### Transport processes

- a) When studying transport processes, we often use the approximation of *steady-state*. Explain what we mean by a system being in steady-state. How would you in a few sentences define what a *flux of particles* is? What is the distinction between a system being in steady-state or being at equilibrium?
- b) Assume that we have a two-phase system and we add a solute,  $s$ , that may partition between the two phases to reach equilibrium. What is the definition of the partition coefficient in terms of the molar fractions,  $x$ , of the solute in the two phases? What is the condition for equilibrium expressed in terms of chemical potentials? Is the partitioning of the solute between the two phases an entropy-driven or an energy-driven process (motivate the answer)?

# Exam June 2012 - Exercise 2

## Transport processes - part 2

c) Particles flow from a reservoir to the left with a concentration,  $c_1$ , through a membrane, and leaves the system to the right with an imposed concentration,  $c_2$  (see figure). Assuming steady-state, draw the concentration profile,  $c(l)$ , where  $l$  is the length of the tube (from left to right). Explain each part of the graph with a few sentences.

